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ABSTRACT: Softwood and hardwood kraft pulps were pretreated with xylanase followed by treatment with hydrogen peroxide, dimethyldioxirane, or hydrogen peroxide reinforced with nitrilamine. The resulting pulps were then further bleached with a DEDED sequence. Bleaching studies demonstrated that the activation of peroxide was an effective method of reducing the total applied charge of chlorine dioxide while still achieving 90+ ISO brightness values. These bleaching studies also demonstrated that softwood kraft pulps responded linearly to the xylanase and peroxide treatments. In contrast, the hardwood pulps exhibited a cooperative interaction between the xylanase treatment and subsequent peroxide-based bleaching treatments. Under optimal conditions these studies suggested a 21% reduction in total applied chlorine dioxide (TAC) charges by pretreating kraft pulps with nitrilamine activated hydrogen peroxide.

KEYWORDS: Bleaching, Kraft Pulp, Xylanase, Dimethyldioxirane, Peroxide, Nitrilamine, Chlorine Dioxide.

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Changes in public policy *(1)* and new market demands *(2)* have increased the interest in developing low effluent AOX bleaching technologies for kraft pulps. In response to these demands, a variety of new pulping and bleaching technologies are being studied. Current solutions to these concerns include the use of extended pulping technologies,*(3)* oxygen deliginification, *(4)* and 100% chlorine dioxide substitution.*(5)* Xylanase pretreatments *(6)* and oxidative alkaline extraction stages *(7)* have also been shown to reduce the levels of AOX generated during the bleaching of kraft pulps. Alternatively the use of ozone as a replacement for chlorine-dioxide has also shown promising laboratory and mill experiences.*(8)*

Despite these significant advances in pulp bleaching technology, there remains a need to develop alternative bleaching protocols which could further reduce the levels of AOX generated from modern chlorine dioxide-based bleaching sequences. Our research interests have been directed towards developing new bleaching technologies which address these needs. Recently we reported that xylanase pretreatments were an effective method of improving the bleaching properties of several non-chlorine based bleaching agents including dimethyldioxirane *(9)* and ozone *(10)*. Xylanase pretreatment of hardwood kraft pulps was shown to enhance the delignification effects of DMD by 11% on kraft hardwoods and 2% on softwood kraft pulp. In this report we have examined the bleaching interactions between xylanase, activated peroxide, and chlorine dioxide for softwood and hardwood kraft pulps.

Experimental

Materials

Oxone™ ($2KHSO_5.KHSO_4.K_2SO_4$), 30% hydrogen peroxide, nitrilamine, acetone, aqueous H_2SO_4, NaOH, and $NaHCO_3$ were all purchased from Aldrich and employed as received. Conventional kraft pulps were prepared in the laboratory from Eastern Canadian hardwood and softwood chips. The softwood kraft pulp had an unbleached kappa number 27.4 and viscosity 37.0 cP. The hardwood kraft pulp had an initial kappa number 18.0 and viscosity 49.5 cP.

A cellulase-free xylanase preparation, prepared by ICI Canada Inc., was employed for all enzymatic treatments. The microbial source for the enzyme was *Streptomyces lividans* [pIAF 20] for the DMD studies and Ecopulp X-200^R for the nitrilamine and hydrogen peroxide studies.

Xylanase and control treatments

Xylanase treatments (X-stage) were carried out on 300 grams (oven-dry weight) of pulp in a Mark II Quantum Mixer at 12% consistency and 50° C. After adjusting the pH of the pulp slurry to 6.0 - 7.0 with 1 N H_2SO_4 the enzyme was added (1 BXIU per gram oven dry pulp) and the mixture was stirred for 2 hours. Control experiments (W-stage) utilized the same experimental approach except that the enzyme was omitted.

DMD pretreatment (I-stage)

A 0.7% charge of DMD was added to the pulp at neutral pH as a 0.1 N DMD/acetone solution at room temperature and at 3.5% consistency. The mixture was stirred for one hour at room temperature before filtering and washing the pulp with water [Note: since the use of DMD for bleaching is currently experimental, all studies were performed following standard laboratory practices for handling peroxides (11)].

Nitrilamine activated peroxide treatment (Pnt-stage)

Pulp samples were placed in polyethylene bags and treated with a 0.9% charge of NaOH, 0.7% charge hydrogen peroxide, and 0.2% nitrilamine. The consistency of the pulp bleaching mixture was 10%. The sealed polyethylene bags were then placed in a 70° C water bath and kneaded every 15 minutes. After two hours the pulp samples were removed, filtered, and washed.

Hydrogen peroxide treatment

The P-stage was executed in the same manner as the Pnt-stage except that the nitrilamine was omitted.

Chlorine dioxide stages

Chlorine-free chlorine dioxide was prepared by calculating the amount of free chlorine in the solution and adding the stoichiometrically equivalent amount of sodium chlorite. All D stages were carried out in sealed glass Mason jars.

The experimental conditions for the 100% substitution stage (D_0) were as follows: consistency, 3.5%; temperature, 50° C; retention time, 30 minutes.

The kappa factors applied are listed below in Table 1.

I. Kappa Factor Employed for Bleaching Softwood and Hardwood Kraft Pulps.

Pretreatment	Kappa Factor	
	Softwood	Hardwood
Control	0.18, 0.20, 0.23	0.16, 0.18, 0.20
Pnt, I, P	0.18, 0.20, 0.22	0.16, 0.18, 0.20
X	0.15, 0.18, 0.20	0.13, 0.16, 0.18, 0.20
XI, X(Pnt), XP	0.16, 0.18, 0.20	0.16, 0.18, 0.20

D_1 charges of 1.2% were applied to pulp samples (20 g.,od weight) under the following conditions: 6% consistency; 70° C; 180 min retention time. D_2 charges of 0.2% were employed for the softwood kraft pulp samples and 0.4% charge for the hardwood kraft pulp samples. The experimental conditions were the same as the D_1 experimental conditions.

Caustic extractions:

Post DMD Stage: The E stage after each DMD treatment was accomplished employing a 1.5% charge of NaOH at 3.5% consistency for 3/4 hr at room temperature.

For DEDED: The E_1 and E_2 stages for the softwood kraft pulps employed 3% and 4% charges of NaOH, respectively. The caustic extractions were performed at 70° C, 60 min retention, and 10% consistency. For the hardwood kraft pulps E_1 and E_2 employed 2% and 0.5% charges of NaOH, respectively. The caustic extractions were performed for 60 min retention at 10% consistency. The E_1 stage was performed at 70° C and the E_2 stage was performed at 73° C.

Pulp properties

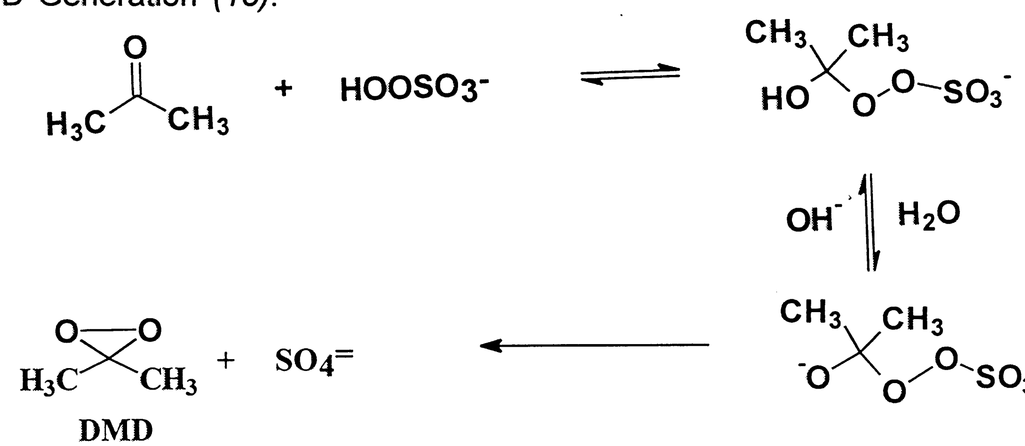
Brightness, Kappa #, and viscosity measurements of the pulp were determined using CPPA standard methods.

Results and discussion

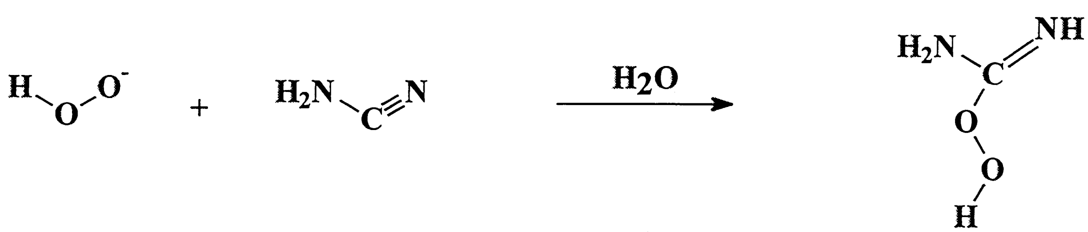
Xylanase/activated peroxide bleaching

Although the benefits of xylanase pretreatment for chlorine dioxide bleaching of kraft pulps are now well established, there application for oxygen-based bleaching protocols is still undergoing active investigation.*(10, 12)* Studies by Eriksson, (12) Joyce (13) and others (14) have clearly highlighted the potential benefits of xylanase pretreatments for ozone and hydrogen peroxide-based bleaching sequences. This report summarizes our preliminary studies directed at evaluating the interactions between xylanase and two forms of activated hydrogen peroxide, dimethyldioxirane and iso-ureaperoxide. The chemical pathways by which these reagents are generated are summarized below.

DMD Generation *(15)*.



Iso-ureaperoxide Generation *(16)*.



The bleaching chemistry of DMD has been explored by Ragauskas *(17)* and Lee et al. *(18)* These promising laboratory studies have been further advanced by a series of pilot-plant trials, which addressed many of the technical issues surrounding mill implementation of DMD. *(19)* Sturm *(16, 20)* and others *(21)* have recently published several articles highlighting the use of nitrilamine reinforced hydrogen peroxide as an improved kraft bleaching agent. These studies demonstrated that nitrilamine activation of hydrogen peroxide for the final stage of bleaching in TCF bleaching sequences resulted in higher brightness values for a given charge of hydrogen peroxide. Recent studies by Troughton have further examined the application of this agent to improve peroxide reinforced oxygen delignification of kraft pulps.(22)

These bleaching agents and other lignin oxidizing treatments will continue to provide new research avenues in the development of low AOX and/or TCF bleaching technologies. This paper describes our research efforts at improving the bleaching properties of DMD and nitrilamine reinforced peroxide by means of coupling their bleaching properties with xylanase pretreatment protocols.

The bio-boosting interactions between xylanase and activated peroxide were examined employing softwood and hardwood kraft pulps. Pulp samples were pretreated with xylanase following well established literature procedures.*(6)* As a control, a second series of pulps was treated in an analogous manner except that the enzyme itself was omitted. The resulting pulps were then bleached with a 0.7% charge of dimethyldioxirane or its molecular equivalence of hydrogen peroxide or hydrogen peroxide/nitrilamine. The results of these bleaching studies are summarized in Table 2. The bleaching results for DMD were reported after an alkaline extraction stage since the I-stage is performed at neutral pH whereas the P and Pnt stages are performed under alkaline conditions. Analysis of the bleaching data from various xylanase/ peroxide treatments indicates that the enzyme-treated hardwood pulps responded more favorably to either the I or Pnt-stages than the softwood pulps. Interestingly, the xylanase pretreatment prior to peroxide bleaching was beneficial to both the hardwood and softwood kraft pulps. A comparison of the bleaching results for WIE versus WPnt for the softwood and the hardwood kraft pulps suggest that the bleaching efficiency of these two agents at low charges is comparable. Indeed, in the case of the softwood kraft pulp it appears that the nitrilamine/peroxide treatment was slightly more effective at delignifying the kraft pulp at these relatively low charges of peroxide.

To explore the bleachability of these pulps each sample was subsequently treated with a DEDED bleach sequence. The kappa factor for the D_{100} stage ranged from 0.13 to 0.23 depending on the exact pulp and these values are summarized in Table 1. The D_1 stage employed a 1.2% charge of chlorine-free chlorine dioxide while the final D_2 stage employed a 0.2% charge of ClO_2 for the softwood pulps and 0.4% for the hardwood pulps. The brightness results for the xylanase/nitrilamine reinforced peroxide studies are summarized in Figures I and II. An examination of these results indicates that the enzymatic pretreatment, combined with the Pnt-stage, significantly raises the brightness ceiling of the pulps. For target brightness values of 89% ISO the use of XI reduces the totally applied chlorine dioxide stage (TAC) by approximately 15 - 23% and even greater reductions were observed at 90% ISO brightness values. A comparison of the nitrilamine-reinforced bleaching studies with the hydrogen peroxide bleaching experiments, summarized in Figures III and IV, further illustrates the benefits of activating hydrogen peroxide with nitrilamine. For both the hardwood and softwood kraft pulps the nitrilamine-reinforced bleaching sequences yielded higher brightness pulps while reducing the TAC employed.

The DMD-treated pulps also afforded higher brightness values at reduced TAC than comparable peroxide bleached pulps, as shown on Figures V and VI. Interestingly, a comparison of the Pnt and DMD treated pulps suggests that the nitrilamine/peroxide treated pulps respond slightly more favorably to the DEDED bleached sequence than the DMD treated pulps. Several factors may be contributing to these differences including the experimental methodology employed to generate DMD for I-stage and differing sensitivity to trace metals present in the pulp. Nonetheless, a comparison of the DMD bleached pulps with the hydrogen peroxide treated pulps demonstrates a clear advantage to activating peroxide prior to bleaching.

Conclusions

In conclusion, the use of activated peroxide species such as DMD or nitrilamine reinforced peroxide followed by DEDED allowed for 2 - 5% ISO brightness gains in hardwoods and 2 - 3% ISO brightness gains for softwood kraft pulps. The use of xylanase pretreatments also improved the delignification properties for all forms of peroxide studied. As previously noted for xylanase/chlorine dioxide bleaching studies, the hardwoods kraft pulps were more responsive to the xylanase treatments than the softwoods which have been attributed to differences in hemicellulose contents between hardwood and softwood kraft pulps.*(23)*

In light of the relative ease of incorporating nitrilamine reinforced peroxide stages in modern bleaching operations we plan to continue exploring the application of X(Pnt) stages as pretreatments for low AOX chlorine dioxide bleaching technologies.

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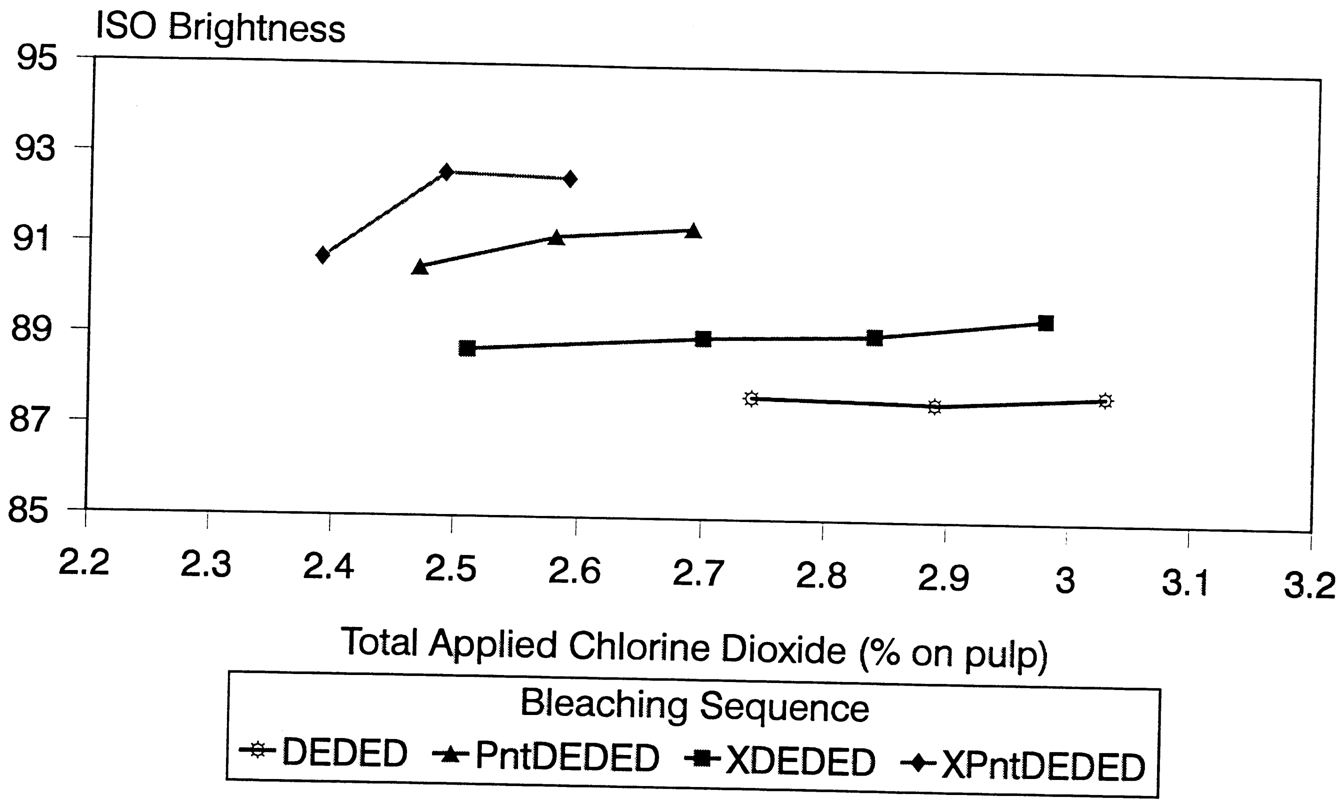
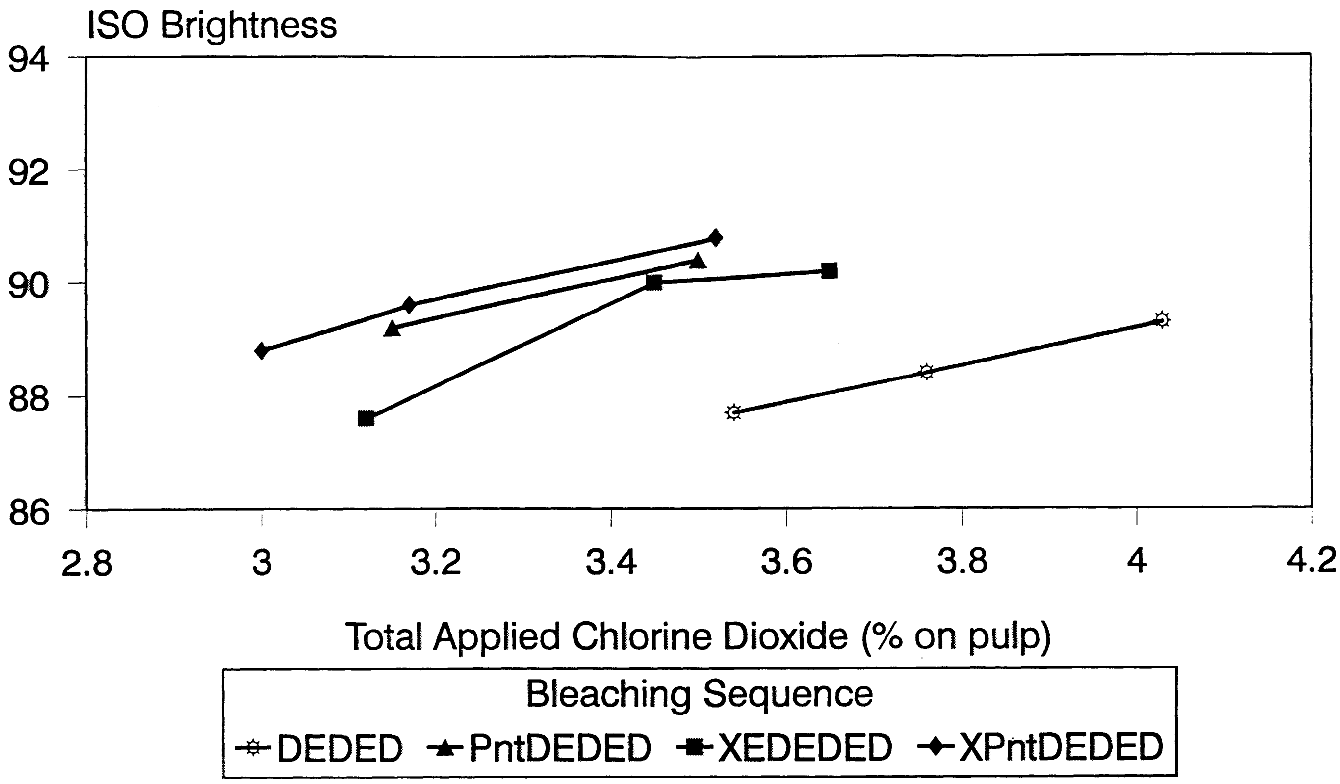
II. Characteristics of Pulp Samples Bleached with DMD, Hydrogen Peroxide, or Nitrilamine/Hydrogen Peroxide.

	Hardwood			Softwood		
Treatment	Brightness (% ISO)	Kappa #	Viscosity (cP)	Brightness (% ISO)	Kappa #	Viscosity (cP)
W	34.7	18.0	49.5	29.7	27.4	37.0
X	35.1	17.3	51.0	30.6	26.7	38.5
WIE	46.4	14.1	40.7	32.3	24.9	35.0
XIE	48.6	13.0	51.0	32.3	24.6	36.6
W(Pnt)	46.1	14.3	38.8	32.6	22.7	25.4
X(Pnt)	46.0	13.0	41.4	32.4	23.0	30.0
WP	41.6	16.0	--	32.9	24.1	--
XP	42.2	14.9	--	32.2	22.7	--

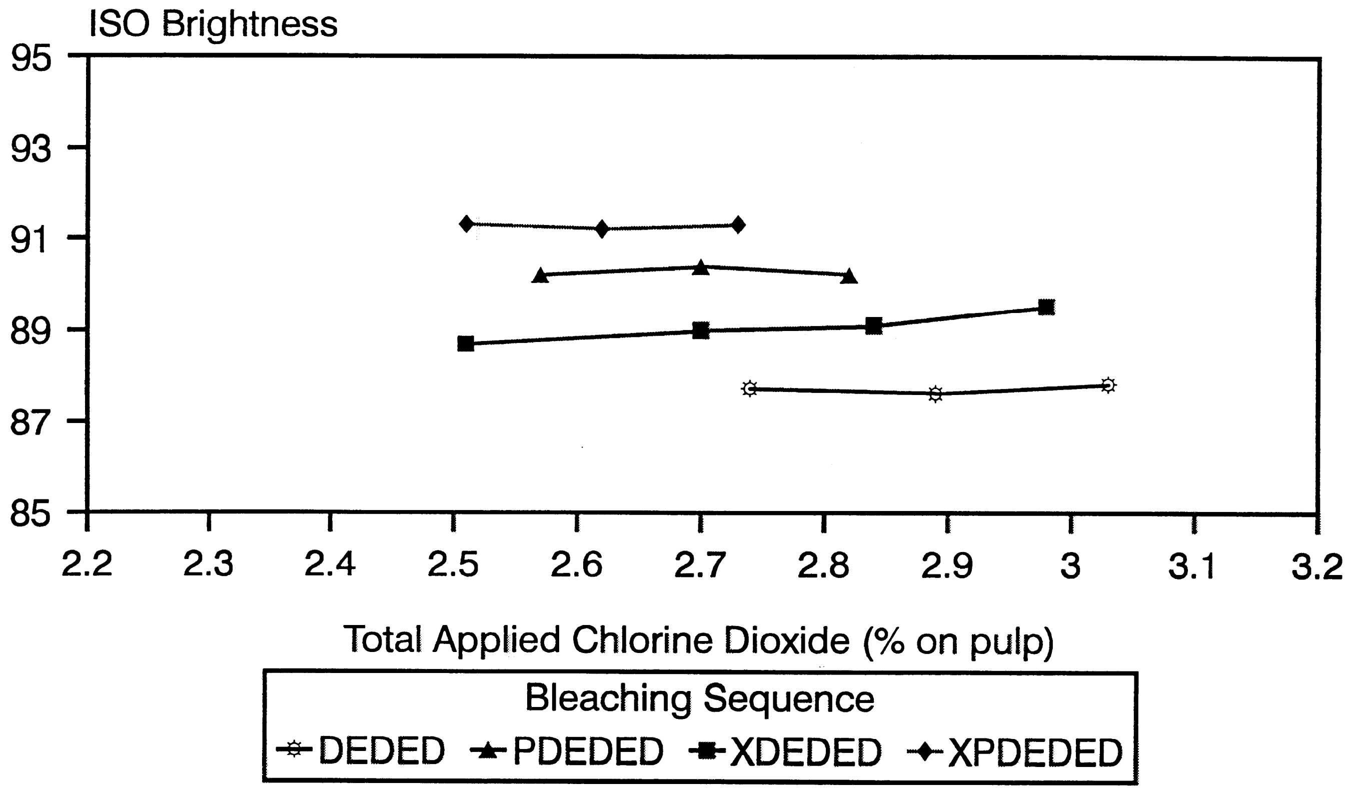
I. Effects of xylanase and nitrilamine-reinforced hydrogen peroxide treatments on DEDED bleaching properties for hardwood kraft pulp.



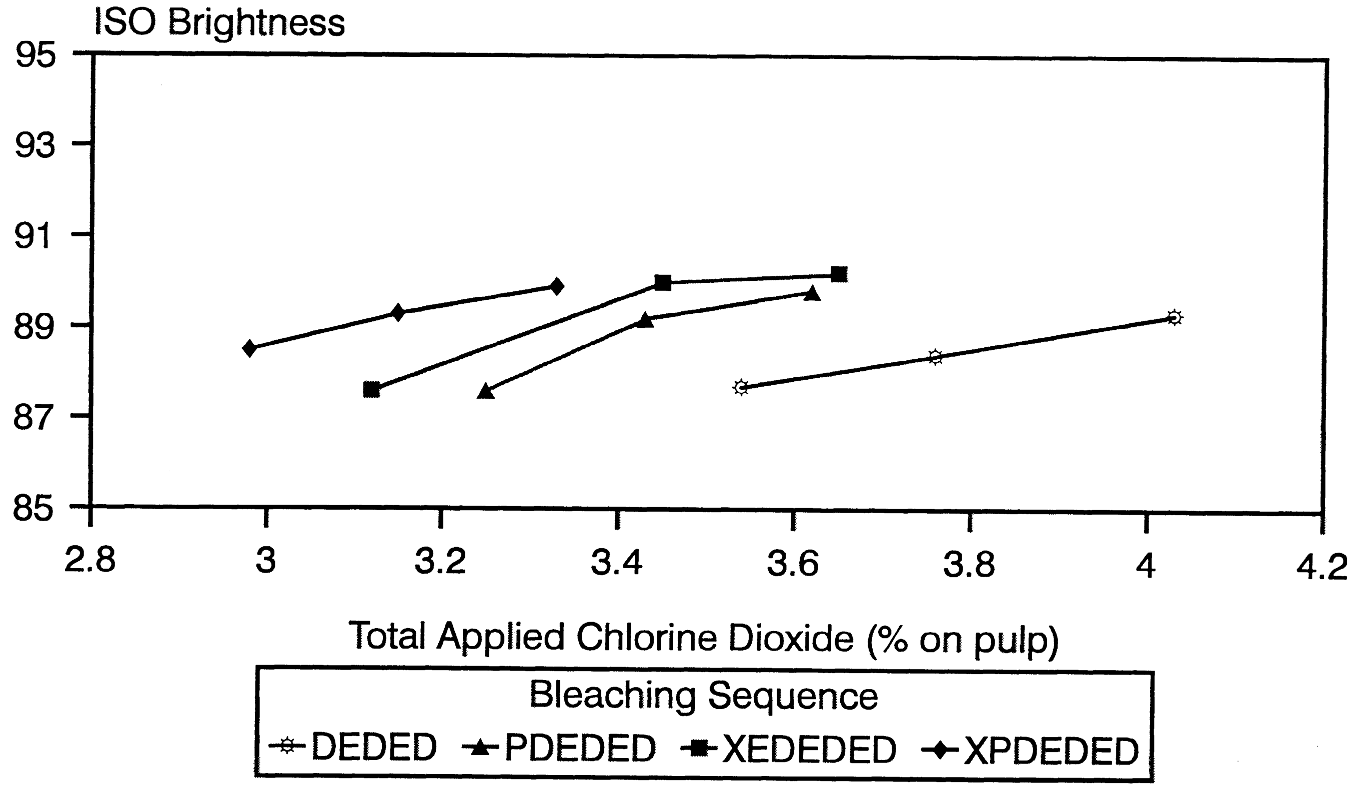
II. Effects of xylanase and nitrilamine-reinforced hydrogen peroxide treatment on DEDED bleaching properties for softwood kraft pulp.



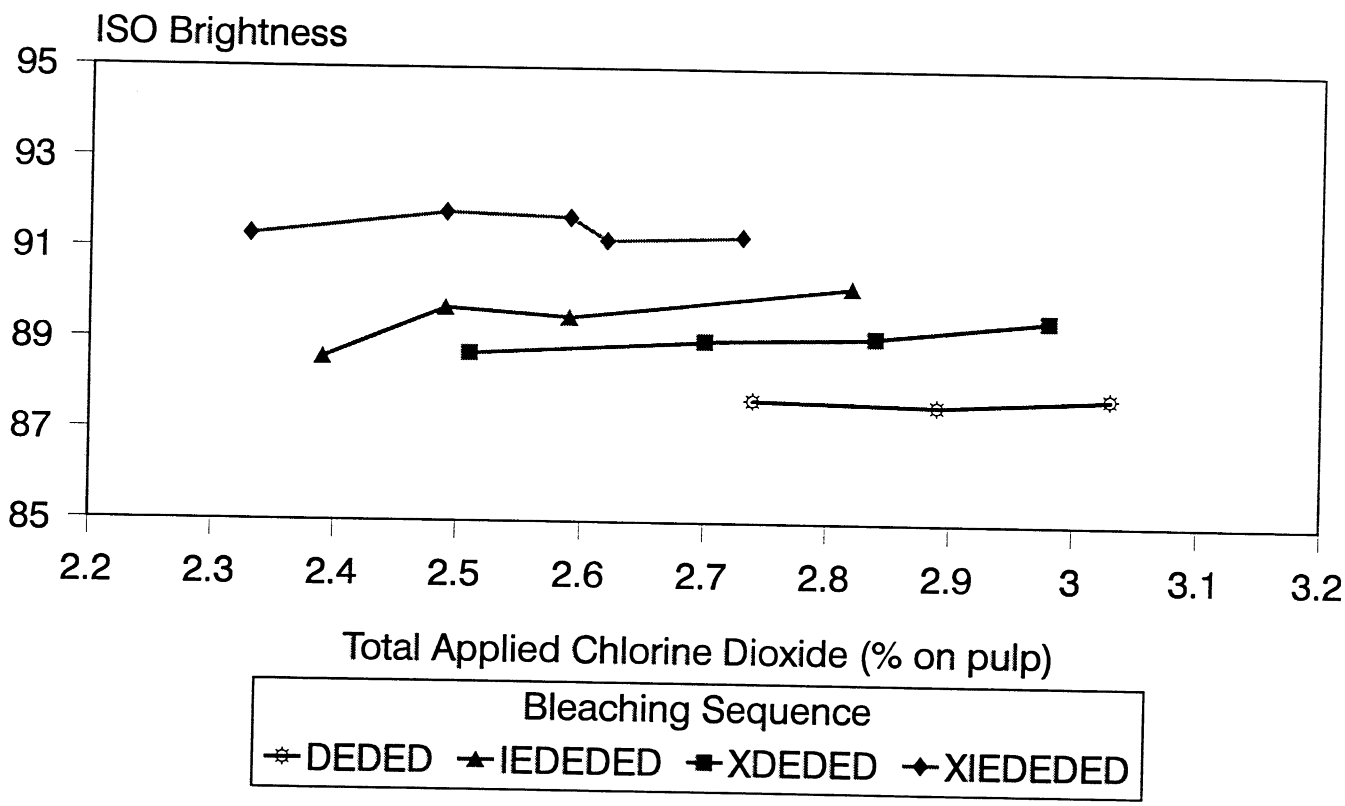
III. Effects of xylanase and hydrogen peroxide treatments on DEDED bleaching properties for hardwood kraft pulp.



IV. Effects of xylanase and hydrogen peroxide treatments on DEDED bleaching properties for softwood kraft pulp.



V. Effects of xylanase and DMD treatments on DEDED bleaching properties for hardwood kraft pulp.



VI. Effects of xylanase and DMD treatments on DEDED bleaching properties for softwood kraft pulp.